$V = \{v_1, v_2 .. v_n\}$

$V = \sum c_i v_i$

since S is orthonormal,

taking dot product of V with any of the vectors in S.

$$V \cdot v_i = c_1 v_1 \cdot v_i + c_2 v_1 \cdot v_i + .. + c_i v_i \cdot v_i + .. + c_n v_n \cdot v_i$$

$$= 0 + 0 + c_i \cdot 1 + .. + 0$$

$$= c_i$$

$$\therefore \boxed{c_i = V \cdot v_i}$$